Sulfur Contamination and Geochemistry of the Florida Everglades:

Review of ACME Findings 1995-2008

Speaker: William H. Orem, U.S. Geological Survey Reston, VA
(703-648-6273; borem@usgs.gov)

Authors: William Orem[1], Cynthia Gilmour[2], David Krabbenhoft[3], George Aiken[4], Anne Bates[1], Harry Lerch[1], and Margo Corum[1]
[1]U.S. Geological Survey, Reston, VA
[2]Smithsonian Environmental Research Center, Edgewater, MD
[3]U.S. Geological Survey, Middleton, WI
[4]U.S. Geological Survey, Boulder, CO

Acknowledgments

Principal Funding: USGS Priority Ecosystems Program for South Florida (G. Ronnie Best, Program Manager 2000-present, Aaron Higer Program Manager 1995-2000)

Other Support: Florida Department of Environmental Protection, South Florida Water Management District, U.S. Environmental Protection Agency, U.S. Fish and Wildlife Service – ARM Loxahatchee National Wildlife Refuge, National Park Service – Everglades National Park and Big Cypress National Preserve, MacArthur Agro-Ecology Research Center

Mesocosms in the Everglades – Central Water Conservation Area 3
These Chambers are Used for Experimental Studies of Contaminants

USGS Sulfur Studies Timeline

- **1995**

-Aquatic Cycling of Mercury in the Everglades (ACME) group begins initial field surveys
-First documentation of high levels of hydrogen sulfide in soil at WCA 2A sites

- **1995-2000 ACME Phase 1 - Intensive field surveys of:**

-sulfur distributions
-sulfur sources and sinks
- links between sulfur and methylmercury production and bioaccumulation in the Everglades

- **2000-2008 ACME Phase 2 – Microcosm and Mesocosm Studies**

-Mesocosm studies of sulfate contamination and methylmercury production and bioaccumulation
-Dry/Rewet microcosm experiments
-Mesocosm studies of sulfur toxicity and internal eutrophication
-Field studies, BCNP, ENP, areas north of Lake Okeechobee

ACME TIMELINE

MESOCOSM Study Details

2000 2001 2002 2003 2004 2005 2006

Hg
F1, U3, Lox, 2BS
2000 – 2001

Hg X SO4 X DOC
3A15, LOX
2001 – 2003

SO4 X Hg X DOC
3A15
2003-2004

Fe(III)
3A15
2005

PO_4 (Newman)
LOX, U3, 3A, TS
2000

S-toxicity
3A15
2003 – 2006

Sulfur Distributions in the Everglades

- About 60% of the Everglades has sulfate concentrations in surface water in excess of background (≤ 1 mg/L)
- Average sulfate concentrations at some marsh sites exceed 60 mg/L
- General decrease in sulfate from north to south across the Everglades
- Distributions of sulfide and other reduced sulfur species in soil generally parallel those for surface water sulfate
- The highest sulfate concentrations are observed in canals within the Everglades Agricultural Area (EAA) – up to 200 mg/L
- Lake Okeechobee and rivers entering the lake have elevated sulfate levels (10-25 mg/L), but not as high as in EAA canals

Sulfate Distributions In Surface Water

> 50 mg/L

~10-50 mg/L

~1-10 mg/L

<1.0 mg/L

Sulfate moves from the EAA and Lake Okeechobee down canals and is discharged into the Everglades through water control structures and breaches in levees

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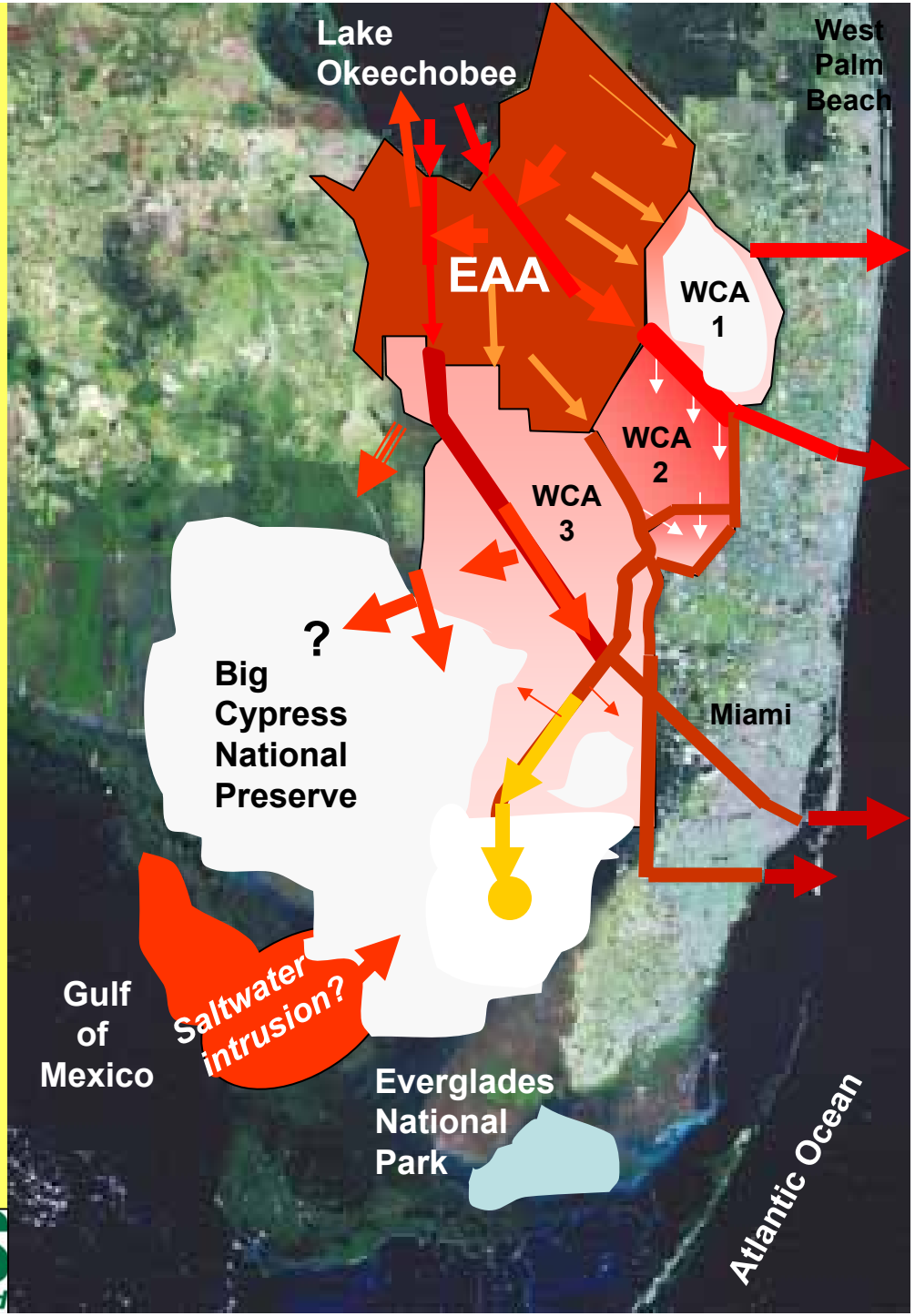

Sources of Sulfate to the Everglades

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- **Concentrations of sulfate in surface water show that canal water draining the Everglades Agricultural Area (EAA) is the principal source of sulfate to Everglades' marshes.**

- **Stable isotope results ($\delta^{34}S$) of sulfate in surface water are consistent with sulfur in fertilizers and soil amendments (new and legacy) used in the EAA as a principal source of the sulfate in the canals.**

- **Deep groundwater (below 9 m depth) has high sulfate concentrations,and could act as a source of sulfate in some areas, however, available geochemical data is not consistent with groundwater as a major source of sulfate to canals or marshes.**

- **Rainwater has low sulfate concentrations (1-2 mg/L), and is not a major contributor to sulfate contamination in the Everglades, but may be the main source of sulfate in pristine areas.**

- **Drought cycles and burns oxidize reduced sulfur stored in soils and remobilize this sulfur as sulfate following rewetting.**

Sugarcane Field in the Everglades Agricultural Area

Sources of Sulfate to Marshes of the Northern Everglades

Water Conservation Area 2A, Site F1

Sulfate from Lake Okeechobee and EAA Fields

precipitation
2.5 mg/l
+5 permil

canal discharge
58 mg/l
+21 permil
$SO_4/Cl = 0.5$

marsh water
55 mg/l
+23 permil
$SO_4/Cl = 0.5$

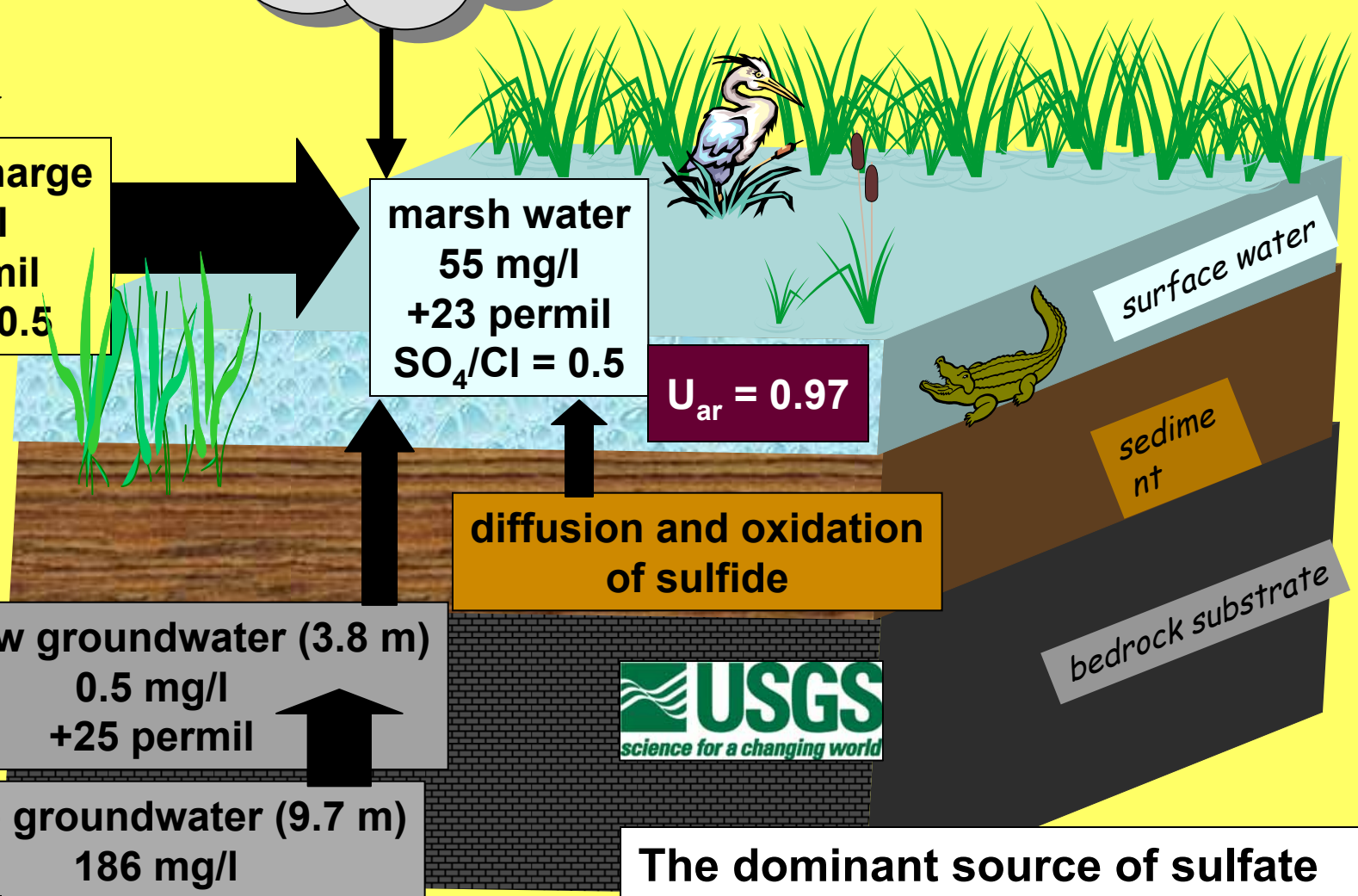
$U_{ar} = 0.97$

diffusion and oxidation of sulfide

shallow groundwater (3.8 m)
0.5 mg/l
+25 permil

deep groundwater (9.7 m)
186 mg/l
+12 permil
$SO_4/Cl = 0.2$

$U_{ar} = 1.30$



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The dominant source of sulfate to Everglades' marshes appears to be canal water discharge.

Effects of Sulfur Contamination on the Everglades:

- Sulfate promotes methylation of mercury to its most toxic and bioaccumulative form: methylmercury

- Sulfide is toxic to plants and animals

- Sulfate promotes release of nutrients from sediments (internal eutrophication)

- Sulfide binds metal ions and sequesters them in soils as metal sulfides

- Sulfate enhances biodegradation of organic soils

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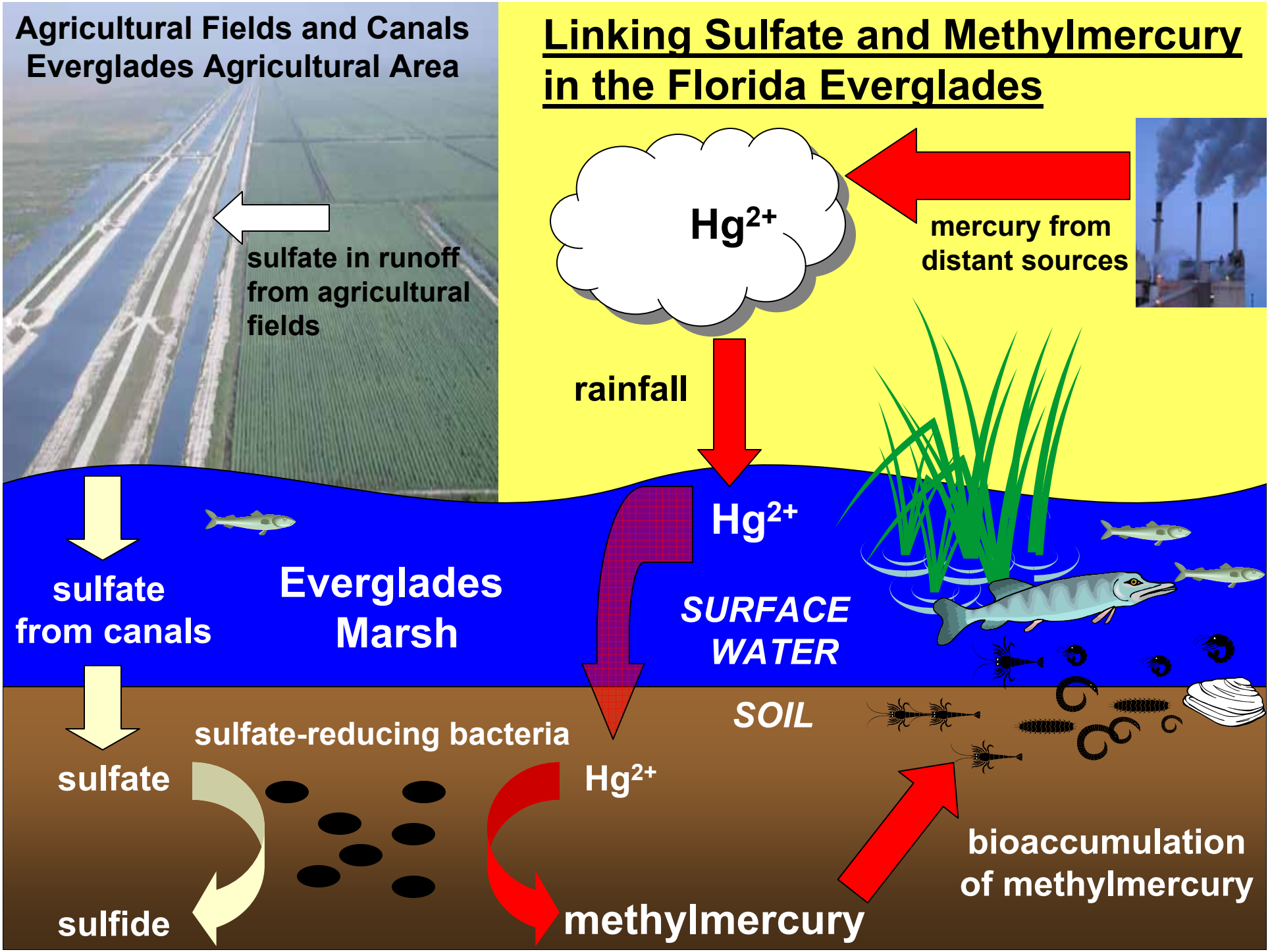
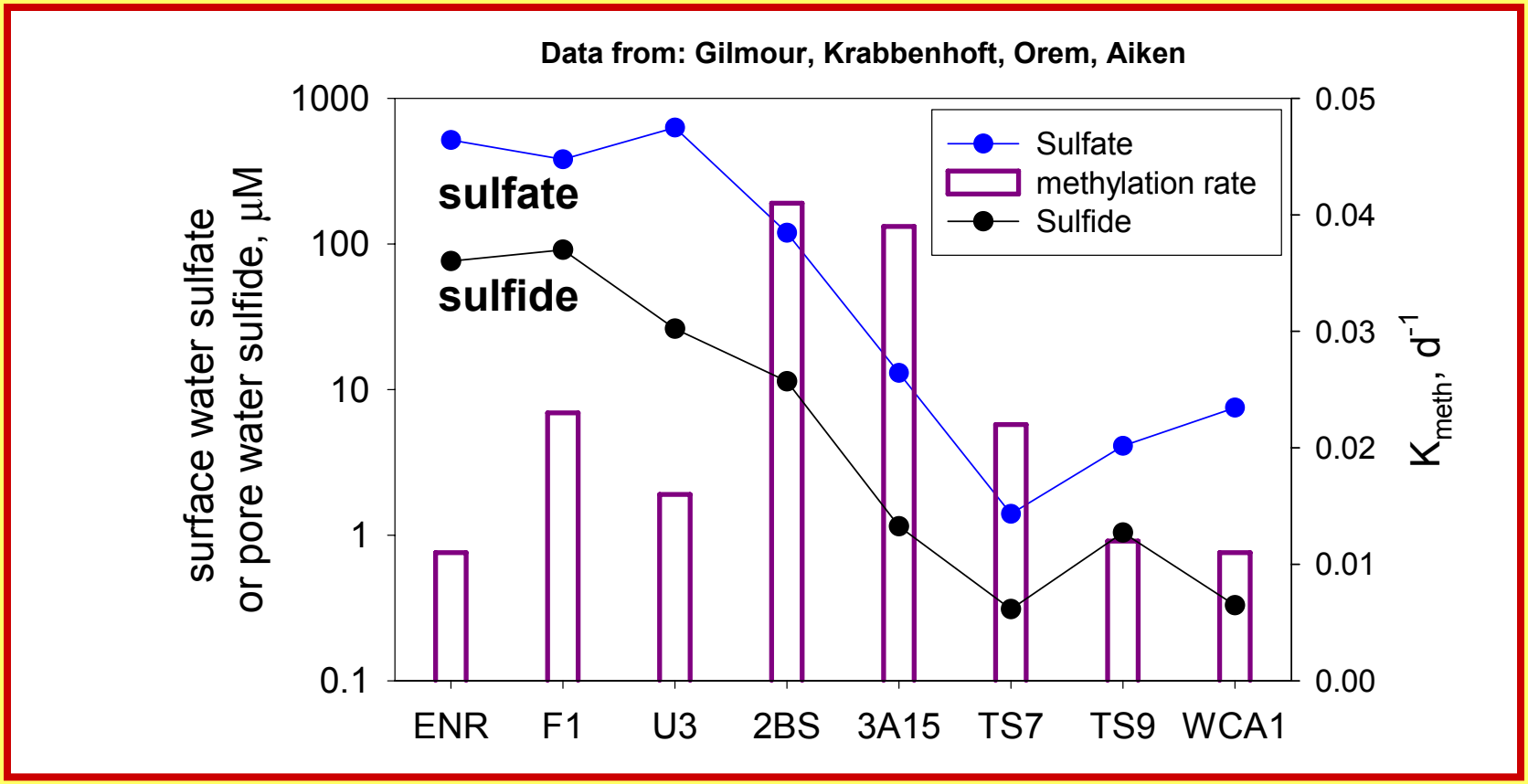

Agricultural Fields and Canals
Everglades Agricultural Area
sulfate in runoff from agricultural fields
Linking Sulfate and Methylmercury in the Florida Everglades
Hg2+
mercury from distant sources
rainfall
Hg2+
sulfate from canals
Everglades Marsh
SURFACE WATER
SOIL
sulfate-reducing bacteria
sulfate
Hg2+
sulfide
methylmercury
bioaccumulation of methylmercury

Relationship Between Sulfate and MeHg

Distributional data across Everglades' sites



- MeHg production increases w/ SO_4 up to at least 100 µM (10 mg/L)
- Methylation declines at porewater sulfide above ~ 20 µM (0.6 mg/L)

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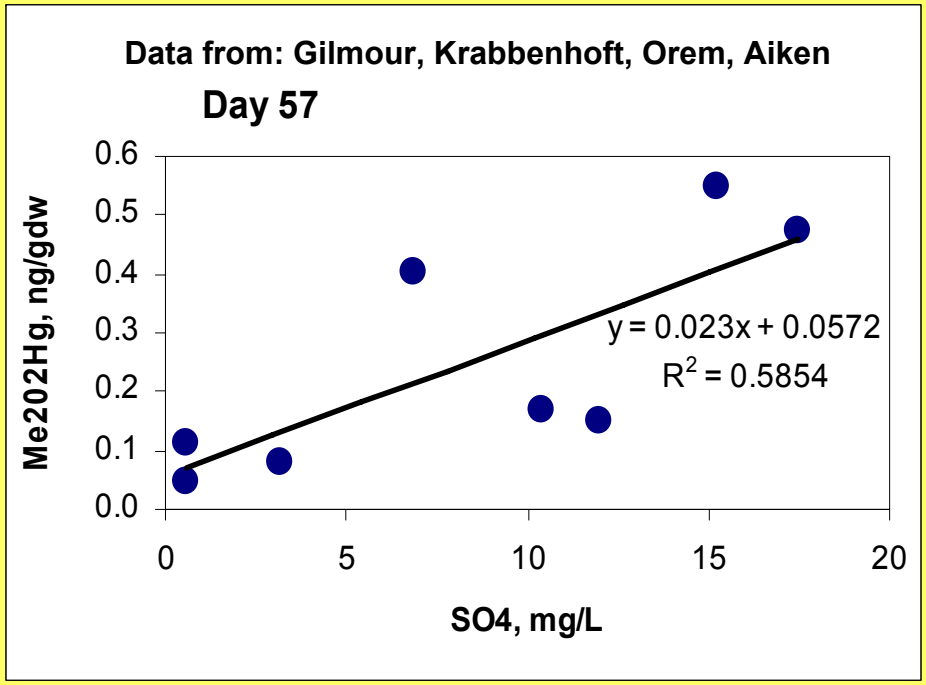
Relationship Between Sulfate and MeHg – Mesocosm Studies

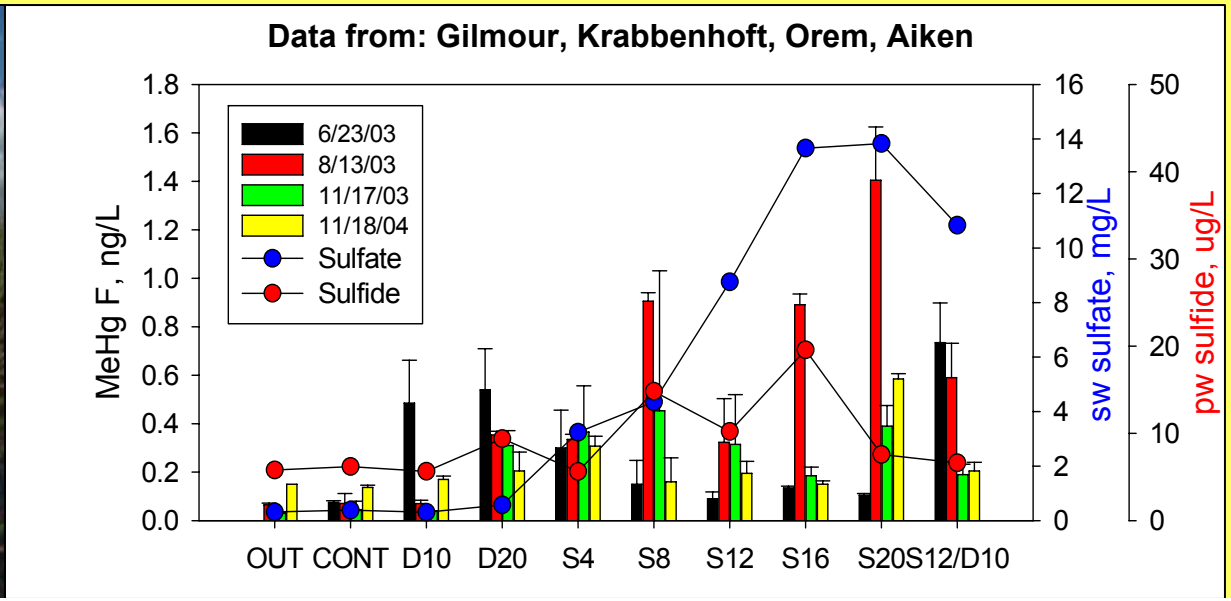


-Add sulfate to Everglades soil and MeHg production increases (confirmed at 5 different sites)

-Linear relationship between sulfate and MeHg production through 20 mg/L

-Sulfide inhibition above 20 mg/L sulfate

-Results confirmed by field, laboratory, and mesocosm data



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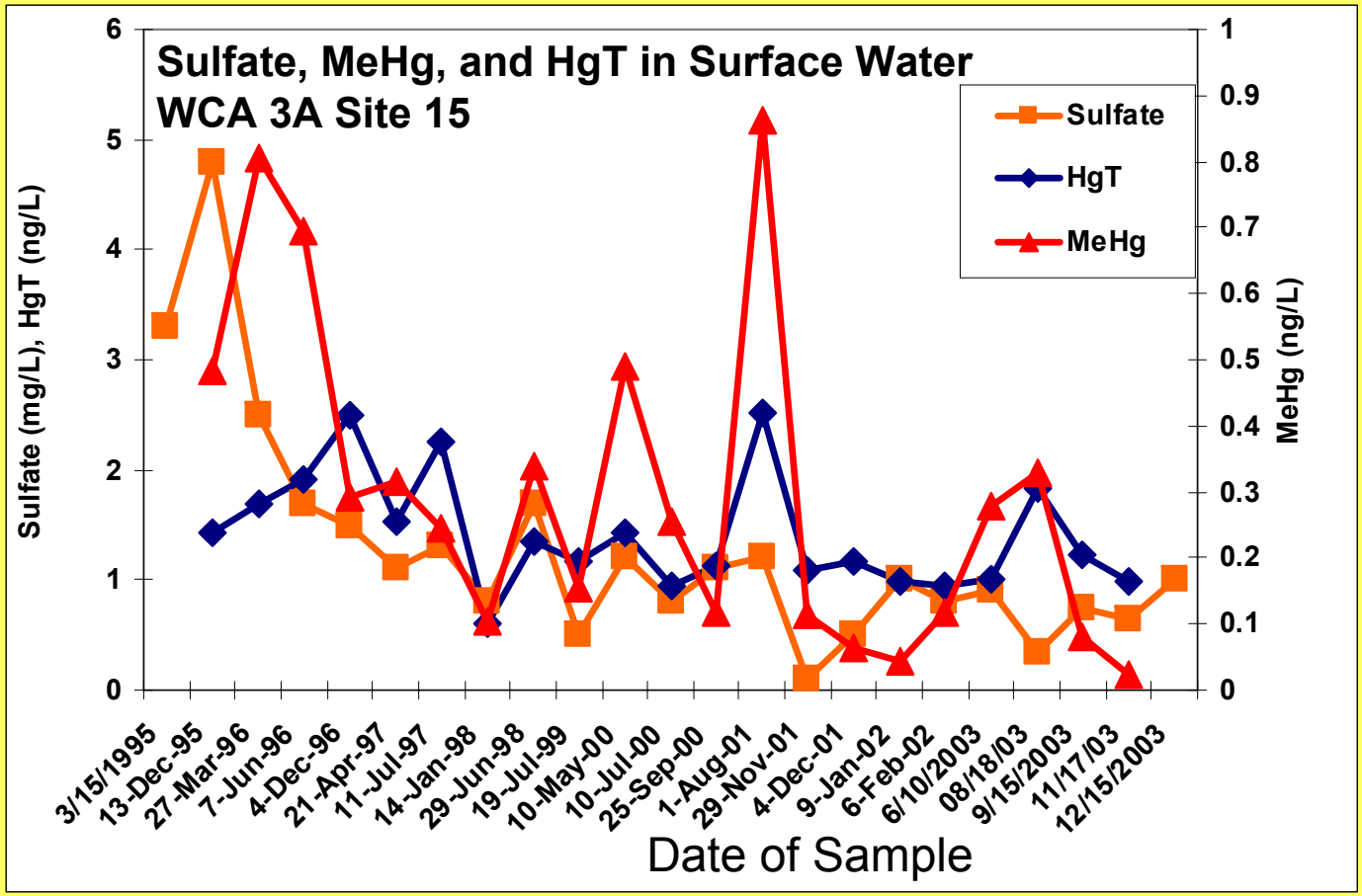
What Happens to MeHg Production in the Everglades if Sulfate Contamination is Reduced??



Changes in sulfate, MeHg, and HgT at a site in the central Everglades (WCA 3A-15) from 1995 to 2003

-**Former MeHg hotspot showed dramatic decline in MeHg over time**

-**Decline not correlated to declines in Hg deposition at this site**

-**Decline closely linked to decline in sulfate at site**

-**Illustrates fast response of ecosystem to declines in sulfate w/r to MeHg production and biopaccumulation**

Everglades – Fire and Drought/Rewet Cycles Effects on Sulfur and Mercury Biogeochemistry

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- Oxidation of organic soil by fire or drought converts reduced sulfur species (organic sulfur and metalsulfides) to sulfate, and releases soil bound mercury and DOC

- After rewet, sulfate is remobilized into water, stimulating microbial sulfate reduction and mercury methylation

- Large amounts of methylmercury may be produced before sulfate is depleted and/or sulfide levels buildup to levels that inhibit methylation

- Effect observed in field studies in the Everglades, in STAs routinely dried down and rewet, and confirmed experimentally in laboratory microcosm experiments

Experimental Dry/Rewet Setup

Background Photo: Fire in Northern WCA 3 – 1999

Desiccated Peat

Mercury and Sulfur - Conclusions

Good News/Bad News

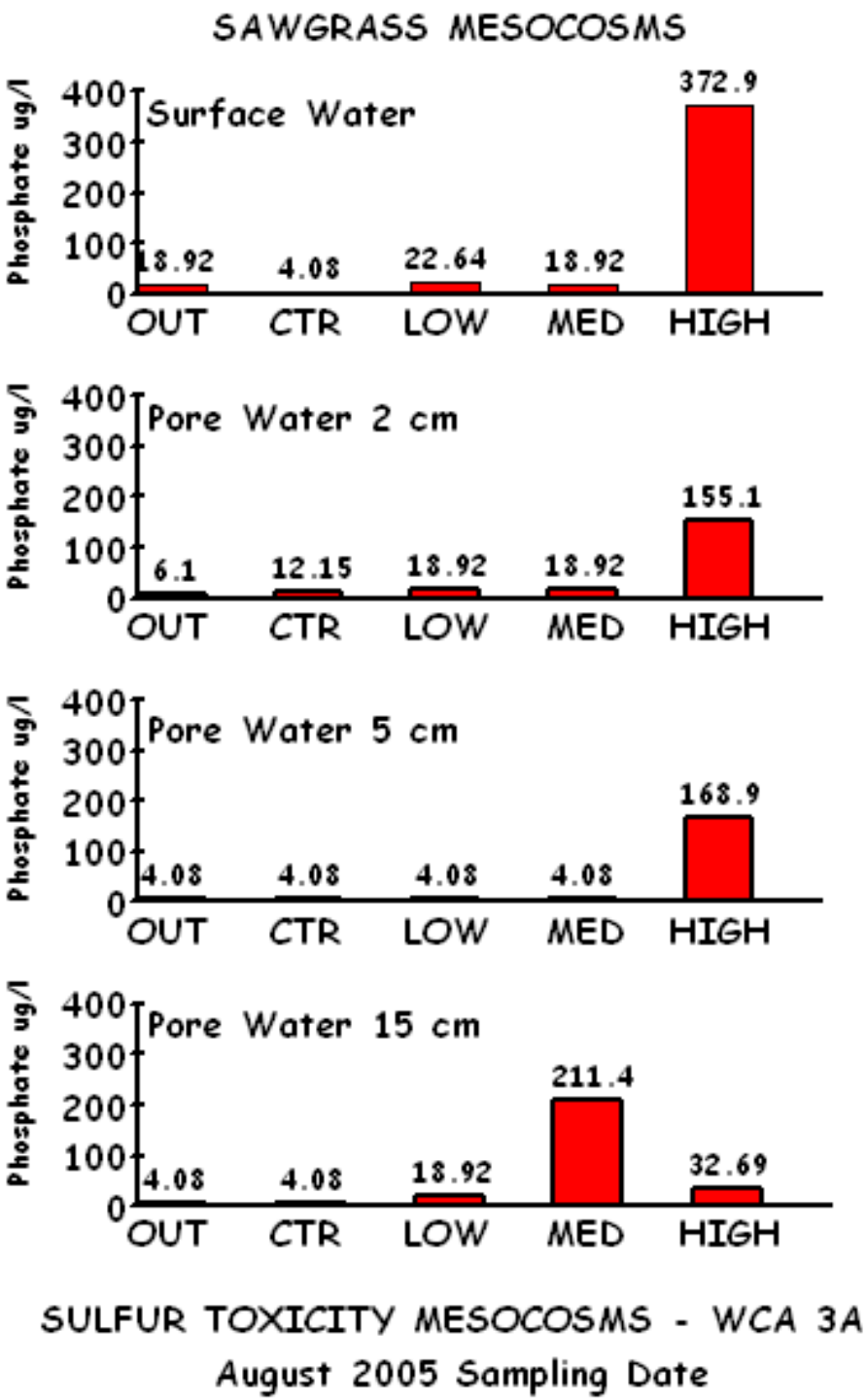
- **Declining sulfate concentrations in central Everglades' marshes have been correlated with declining MeHg in fish, water and soil.**

- **Other areas of the ecosystem (notably ENP) appear to have increasing levels of MeHg in fish**

- **Sulfate concentrations in most canals are not dropping; and sulfate-laden water is delivered in ENP via a major canal**

- **Reducing sulfate loads to the ecosystem provides a mechanism for limiting MeHg production in the Everglades**

- **Restoration plans to increase the amount of water delivered to the Everglades could increase overall sulfate loads and move sulfate farther into the ecosystem**



Sulfate Contamination and Internal Eutrophication

Sulfate addition to mesocosms results in:

-buildup of sulfide from microbial sulfate reduction

-large decrease in soil redox conditions (more reducing conditions)

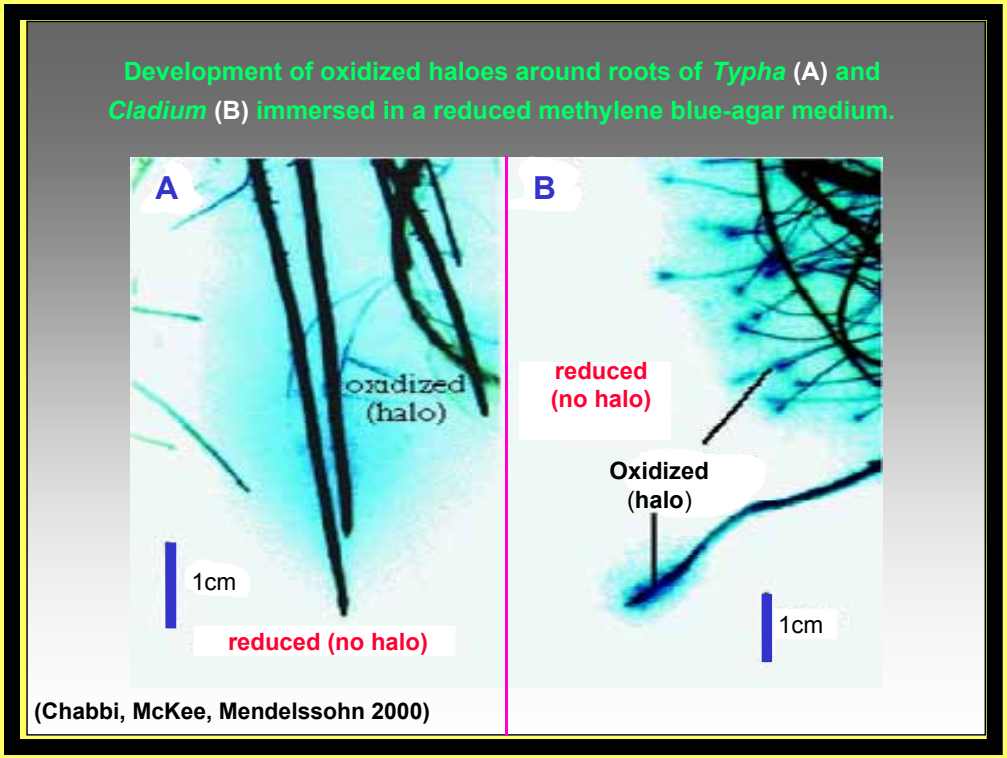
-remobilization of phosphorus, ammonium, DOC, and DON (phosphorus release up to 50x higher in dosed mesos compared to controls) is shown at left

-destabilization of organic soils, mechanism not well understood

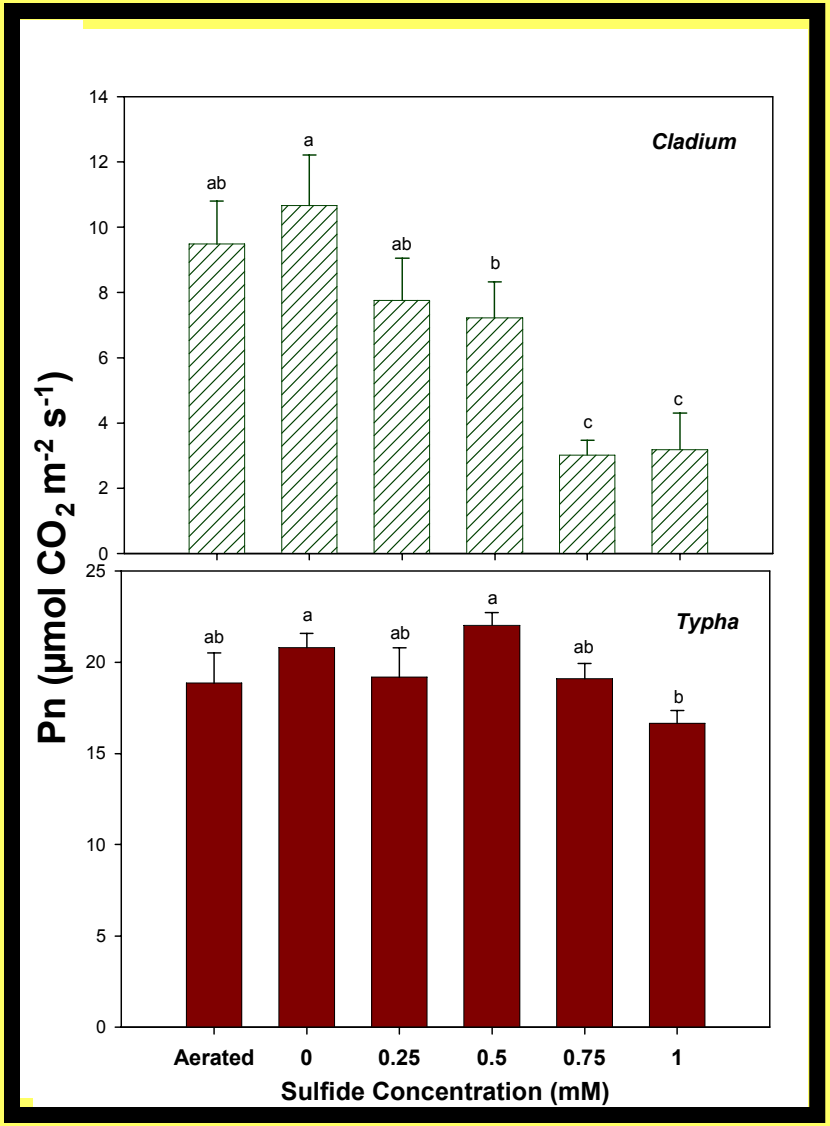
Impacts of Sulfide on Macrophyte Growth

Li, Mendelssohn, Chen, and Orem
Freshwater Biology, in review

- *Cladium* oxidized zone only at root tips *Typha* oxidized zone all along root axis.



- Sawgrass (Cladium) more sensitiveto to sulfide toxicity than cattail (Typha) sulfide levels >9 ppm



Conclusions

Sulfate is a Major Water Quality Problem for Everglades Restoration

- -widely distributed contaminant
- -sources: agriculture, soil oxidation, Lake Okeechobee
- -key control on methylmercury production
- -sulfur and mercury issues exacerbated by natural and unnatural dry/rewet cycles
- -promotes eutrophication by causing release of P and N from soil
- -sulfide is toxic to native flora and fauna
- -sulfate may cause destabilization of organic soils

Approaches to Reduce Sulfur Loads to the Everglades

- Reduce current sulfur use in the Everglades Agricultural Area (EAA) to the minimum needed to sustain crop yields

- Reduce use of sulfur-containing fungicides

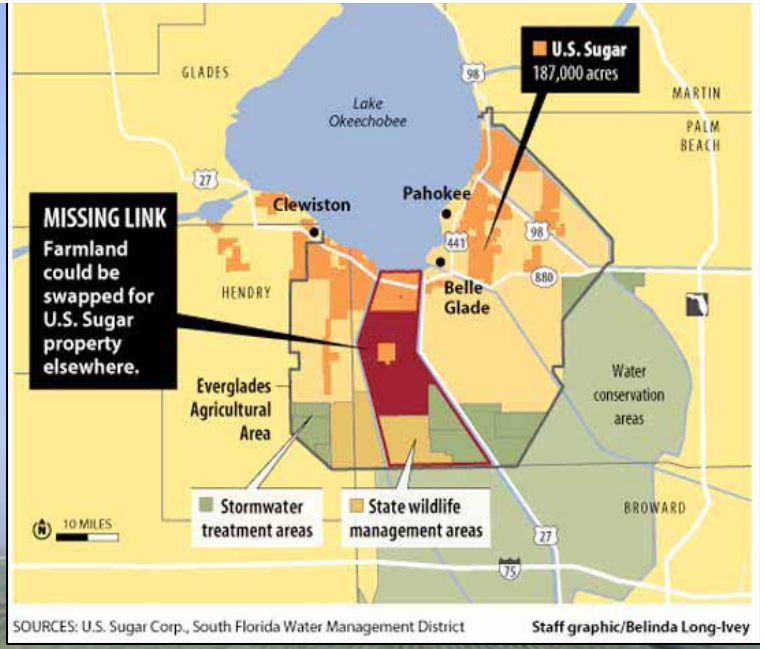
- Redesign existing Stormwater Treatment Areas (STAs) to improve removal of sulfate from water:
  - -examine sulfate removal by PASTAs
  - -pass contaminated water through limestone and feldspar as an initial removal process
  - -consider use of large anaerobic bioreactors or PRBs for microbial removal of sulfate (add iron for sequestration)
  - -greatly increase residence time of water in STAs
  - -consider use of genetically engineered wetland plants in STAs that utilize and store higher amounts of sulfate

- Avoid the use of canals for the delivery of additional water to protected areas like ENP, BCNP, LNWR; instead use sheet flow over the large Water Conservation Areas that provides a final sulfate-removal buffer

Photo: Storm Water Treatment Areas (STA's) in South Florida

EAA Land Purchase and Sulfur Issue

- Land purchase should reduce overall sulfur loads to the Everglades by:
  - -taking land out of cultivation and reducing overall sulfur applications
  - -reducing soil oxidation in the flooded parts of the EAA, and sequestering sulfur in the soil



- Initial flooding will likely result in a large flux of sulfate, phosphorus, and other contaminants; this will need to be monitored carefully and managers should avoid discharge of this initial plume into the ecosystem

- Due to soil oxidation in the EAA and resulting differences in elevation between the Lake, the EAA land, and the Everglades, ponding of the area is likely – from the standpoint of sulfur contamination this could be helpful:
  - -slow flow will allow microbial sulfate reduction to reduce most of the sulfate to sulfide, and allow for sequestration of sulfur as organic sulfur and metal sulfides in soil

The Sulfur Issue - Unanswered Questions

- What is the mass balance of sulfur entering the ecosystem?
  - -current agricultural applications
  - -soil oxidation (legacy sulfur)
  - -groundwater
  - -other sources

- Does sulfate contamination impact the STAs ability to sequester phosphorus, as well as impacting eutrophication across the ecosystem?

- Does sulfide toxicity impact other organisms in the ecosystem?

- Will increased water flow affect sulfate loads to ENP, BCNP, LNWR, and other sensitive areas? How will restoration of sheet flow impact sulfate loads across the Everglades?

- How will the proposed U.S. Sugar land purchase and connection of Lake Okeechobee to the Everglades impact sulfate loads, and Everglades' biogeochemical processes linked to sulfur?

Thank You for Your Attention!

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Mid Taylor Slough – Everglades National Park